OPPORTUNITIES FOR TECHNOLOGICAL ADVANCES IN THE CONVERSION OF NATURAL GAS TO LIQUID FUELS AND CHEMICALS.

Imre Puskas
Research Services
939 Brighton Drive
Wheaton, IL. 60187

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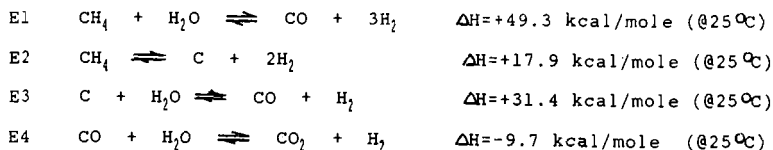
INTRODUCTION.

Natural gas is a premium fuel because of its high heating value (210.8 kcal/g-mole methane) and clean burning characteristics. However, transportation costs from source to market may prevent its fuel use. Alternative uses of natural gas are conversions to chemicals and liquid fuels. Natural gas is the favored starting material for ammonia and methanol. Natural gas can also be converted to easily transportable liquid fuels. However, conversions to alternative fuels with lower heating values (~156-167 kcal/carbon atom for hydrocarbons; 170.9 kcal/g-mole for methanol) can be rational and economical only under special circumstances.

Excellent reviews are available by Rostrup-Nielsen (1), Fox (2), Mills (3), Fierro (4), Lunsford (5), Kuo et al. (6), and by many others on the research and development status of the natural gas conversion technologies. By comparing salient chemical, technological, historical and economic features of the major conversion technologies, this study is an attempt to define the best opportunities for further technological advances.
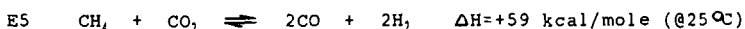
SYNTHESIS GAS FROM NATURAL GAS.

Synthesis gas is a common intermediate in the syntheses of ammonia, methanol and synthetic crude. Natural gas can be converted to synthesis gas by three different reactions: 1./ Steam reforming. 2./ Reforming by carbon dioxide. 3./ Partial oxidations.

Steam reforming. The overall reaction is shown by Equation 1 (E1). This reaction takes place in two steps. First methane is decomposed to carbon and hydrogen (E2), which is followed by a carbon-steam reaction (E3). All three reactions are endothermic equilibrium reactions and require high temperatures for favorable equilibria. During steam reforming, the water gas shift reaction (E4) is an inevitable side reaction. This latter is exothermic; its equilibrium is shifted to its reversal (i.e. to the left) by increasing temperature. Steam reforming requires a catalyst. Nickel on alumina is used most widely. The temperature of most of the reformers is in the 730-860 °C range. Steam is used in large excess (2-5 fold) for faster rates and to prevent carbon build-up on the catalyst.

$$E1 \quad CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = +49.3 \text{ kcal/mole (@25°C)}$$

$$E2 \quad CH_4 \rightleftharpoons C + 2H_2 \qquad \Delta H = +17.9 \text{ kcal/mole (@25°C)}$$

$$E3 \quad C + H_2O \rightleftharpoons CO + H_2 \qquad \Delta H = +31.4 \text{ kcal/mole (@25°C)}$$

$$E4 \quad CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -9.7 \text{ kcal/mole (@25°C)}$$
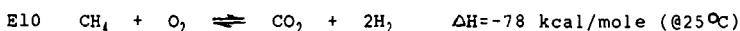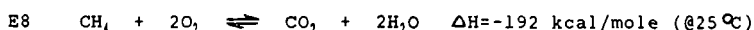
Review articles (7-10) provide details on the chemistry and technology of methane steam reforming. Some aspects are highlighted here. Kinetic evidence suggests that the reaction rate is controlled by diffusion. Steam reforming is carried out in furnaces which contain parallel catalyst tubes made of HK-40 alloy (25% Cr, 20% Ni, 0.35-0.45% C). The tubes are designed for a minimum life of 10 years. Inside the tubes is the catalyst. The tubes are heated from the outside by burners. Reforming pressure on the tube side can be as high as 500 psi. Since natural gas is usually available under high pressure, reforming under pressure can result in substantial savings in downstream compression costs if compressed synthesis gas is needed. Due to improved heat recovery and efficient energy management, current steam reformers operate with good thermal efficiency (11-12).

Carbon dioxide reforming. This reaction has much resemblance to steam reforming. The overall reaction is illustrated by E5. It is

E5 $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ $\Delta H=+59$ kcal/mole (@25°C)

E6 $C + CO_2 \rightleftharpoons 2CO$ $\Delta H=+41.2$ kcal/mole (@25°C)

highly endothermic. It occurs in two separate steps, the first step being methane decomposition (E2). In a subsequent step, the carbon is gasified by carbon dioxide (E6). The reverse reaction of E6 is the Boudouard reaction, which can be a source of carbon deposition. Carbon dioxide reforming, as indicated by E5, cannot be practiced commercially because the carbon gasification by E6 is not fast enough to prevent carbon accumulation. Steam addition to the feed is required for successful operations. Commercial interest in carbon dioxide reforming originates from the need for synthesis gas compositions with low H_2 to CO ratios. Haldor-Topsoe (13,14) and Calorific GmbH (15) reported on process developments. The Midrex-Process for the reduction of iron ores generates syngas essentially by carbon dioxide reforming with low steam usage (16).

Partial oxidation. Controlled reaction of methane with oxygen can give good yield of synthesis gas. The desired reaction is shown by E7. However, early studies (17) have already revealed, that even if a 2:1 molar mixture of methane and oxygen is reacted, the initial reaction is complete burning (E8) and incomplete burning (E9 and E10). These are very fast reactions, requiring only milliseconds. Following the initial fast reactions, the unreacted methane reacts with steam and carbon dioxide generated by the reactions E8-E10. However, these reforming reactions are slower

E7 $CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2$ $\Delta H=-8.5$ kcal/mole (@25°C)

E8 $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ $\Delta H=-192$ kcal/mole (@25°C)

E9 $CH_4 + 1.5O_2 \rightleftharpoons CO + 2H_2O$ $\Delta H=-124$ kcal/mole (@25°C)

E10 $CH_4 + O_2 \rightleftharpoons CO_2 + 2H_2$ $\Delta H=-78$ kcal/mole (@25°C)

by more than an order of magnitude. The reaction temperature depends on the preheat temperature of the reagents. Mixing occurs in a burner. A flame is spontaneously produced with adequate preheat, even though at room temperature the composition would be non-flammable. Outside the flame, the temperature quickly falls due to the endothermic reforming reactions. The reactor is a refractory-lined vessel. The first commercial installation of a non-catalytic partial oxidation unit using 95% pure oxygen was in the Brownsville synthetic fuel plant in 1950, operating at 425 psi (18). The new synfuel plant in Malaysia designed by Shell International Gas Ltd. uses a similar process (19).

Partial oxidation can be conducted catalytically. The catalyst maintains the reaction without a flame, and accelerates the slower reforming reactions to establish thermodynamic equilibria. However, truly catalytic partial oxidations have been restricted mostly to laboratory studies (20). Most of the commercial "catalytic partial oxidation" processes consist of a sequence of non-catalytic partial oxidation and catalytic reforming. Synthesis gas generation for copper smelters may involve truly catalytic partial oxidation (21).

The oxidant in the partial oxidation processes can be air or pure oxygen. In case of air use, the nitrogen appears in the synthesis gas as a diluent.

Combined reforming. Steam reforming, carbon dioxide reforming and partial oxidation supply synthesis gas with greatly differing composition. The H_2/CO ratios from the three processes are >3, <1 and <2, respectively. Combination of the various processes can lead to the desired synthesis gas compositions. Furthermore, combination of steam reforming and partial oxidation also led to the development of more energy-efficient reactors and processes. These advances came from BASF (22), Haldor-Topsoe (23), Lurgi (24), ICI (25) and Uhde GmbH (26), etc. A recent review by Orphanides (27) gives more detail on the progress. Some of the advances will be illustrated by specific examples:

For ammonia synthesis, hydrogen is required rather than synthesis gas. The CO content of the synthesis gas is converted to hydrogen and carbon dioxide by the water gas shift reaction (E4). In newer ammonia plants, the steam reforming furnaces have been replaced by two reactors (Figure 1). The first reactor is the "Gas Heated Reformer" (GHR) where about 75% of the methane is reformed to synthesis gas around 700°C and up to 600 psia. The heat for the reforming is supplied by the effluent gases of the second reactor. This latter one is an "autothermal reformer" which converts the residual methane of the first reactor effluent by partial catalytic air oxidation. This combination has the following benefits: 1./ It introduces the nitrogen required in the ammonia synthesis step. 2./ It generates heat in the second reactor which is very efficiently utilized in the first reactor and eliminates the need for the bulky steam reformer furnaces. Heat transfer in the GHR is much better than in the old furnaces because both sides of the exchanger tubes are under pressure. In some of the newer ammonia plants, a single reformer replaces the two reactors of Figure 1 (as in Figure 2).

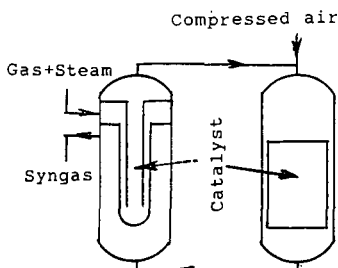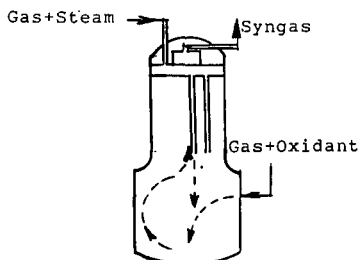Figure 1. Combined Reforming.   Figure 2. Schematic Showing of a Combined Autothermal Reformer.

The synthesis gas generated by the conventional steam reforming furnaces is acceptable for methanol synthesis even though the hydrogen content is too high. The combined reforming concept shown in Figure 1 is also applicable to methanol synthesis if pure oxygen is the oxidant in the second reformer. According to Lurgi (24), the process economics are more favorable for the combined reforming option because of improved methane to methanol conversion efficiency. The Combined Autothermal Reformer (CAR) (Figure 2) currently under development by Uhde GmbH (26) appears attractive for the next generation methanol plants.

If inexpensive carbon dioxide is available at the site of the methanol plant, a combination of steam reforming (E1) and carbon dioxide reforming (E5) results in more favorable synthesis gas composition and also in higher methane-based conversion efficiency to methanol. For these reasons, natural gas sources with 10-30% carbon dioxide content might be particularly favored for methanol synthesis. Indeed, good methanol yield was reported from the CO_2-containing gas fields of New Zealand (28-29).

AMMONIA SYNTHESIS.

Ammonia production from hydrogen and nitrogen was pioneered by Haber and Bosch in 1913. This led to the development of the giant ammonia industry which provides fertilizer to agriculture to feed the growing world population. Ammonia is one of the largest volume chemicals. World production is estimated at 110 MM tons per annum. About 84% of the production goes to fertilizers. Ammonia prices during the last fifteen years ranged from less than $100/ton to $350/ton due to variations in supply and demand.

Scheme 1. Ammonia Synthesis from Natural Gas and Air.

Natural gas purification	Combined reforming	Shift reaction	CO_2 removal	Gas puri- fications	Com- pression	NH_3 loop

Scheme 1 illustrates the process steps involved in ammonia synthesis starting with natural gas (7). The ammonia synthesis step is shown by E11. The reaction is exothermic and leads to equilibrium. The synthesis is conducted at 2000-5000 psi and

E11 $3H_2 + N_2 \rightleftharpoons 2NH_3$ $\Delta H=-26$ kcal/2moles of NH_3

475-500°C over an alkalized, promoted magnetite catalyst. About
13-16% conversion is obtained in commercial recycle operations,
with 100% selectivity to ammonia. The ammonia is recovered by
condensation after refrigerating the gas stream. A small purge
stream is taken from the synthesis loop to prevent inert buildup.
Two kinds of converter designs are in commercial use: tubular and
multiple bed. Recent developments in the synthesis loop include
more efficient converter designs (30) and the introduction of
magnetite-ruthenium catalyst combination for higher conversion
(31). The largest ammonia plants have 1800 t/d capacity.

During the last two decades, the economics of ammonia production
have substantially improved due extensive modernization programs.
The progress is reflected by reduction of the energy requirements
(i.e. the heating value of the feed including fuel use) per ton
of ammonia from about 36 GJ to about 28 GJ. The overall process
efficiency based on E12 is about 82%.

E12 $CH_4 + 1.3974\ H_2O + 0.3013\ O_2 + 1.132\ N_2 \rightarrow CO_2 + 2.264\ NH_3$
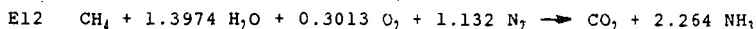
METHANOL SYNTHESIS.

Synthetic methanol has become available in 1923. Currently
worldwide production is approaching 30 MM ton per annum. Nearly
half goes for formaldehyde synthesis, which represents a
declining market. Other uses include acetic acid synthesis,
synthesis of methyl esters, solvent use and recently methyl t-
butyl ether (MTBE) synthesis. This latter use is rapidly growing
because MTBE is the most preferred octane booster for
reformulated gasoline. In recent years, possible "clean fuel" use
of methanol was also widely studied (32). The energy crises of
the seventies motivated broad range of scientific research in
methanol-related subjects as indicated by review articles (33-
37). In the last two decades, large capacity plants were
constructed near to inexpensive gas sources, exerting a downward
trend on methanol prices. During the last decade prices ranged
between $0.35-0.75/gal until a recent escalation to above $1/gal.

E13 $2H_2 + CO \rightleftharpoons CH_3OH$ $\Delta H=-21.7$ kcal/mole (@25°C)

The synthesis gas from the reformer requires water removal and
compression before methanol synthesis. The synthesis (E13) is an
exothermic equilibrium reaction. The original catalyst was zinc-
chromium oxide which required high temperatures and pressures.
Since the late sixties, copper-zinc oxide catalysts have been
adopted which function well at much lower temperature and
pressure (230-270°C; 700-2000 psi). The reactors in commercial
service are either of the "quench type" or exchanger type; slurry
reactors have also been piloted. Synthesis gas conversion is
about 15% per pass, but the methanol concentration is only 4-7 %
because of accumulation of inerts and excess reagents in the
recycle loop. After cooling, the methanol is condensed from the
reactor effluent; the gases are recompressed and recycled. A
purge stream is taken from the recycle loop which is rich in
hydrogen if steam reforming is the source of synthesis gas.
Methanol can be obtained in up to 98-99% selectivity. Ethers,
aldehydes, ketones, esters, water, higher alcohols, methane and
hydrocarbons are the by-products. The energy requirements for the
various natural-gas based methanol processes are estimated at
32.4-35.3 GJ/ton methanol, corresponding to 78-85% carbon based
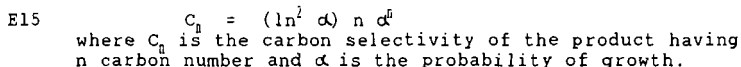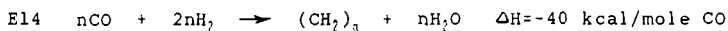efficiency.

Recent research and development efforts on methanol appear to
have two different directions: 1./ Finding improved catalysts
(35, 38-39). 2./ Increasing conversions to methanol by shifting
the equilibrium (40-44).

HYDROCARBONS VIA FISCHER-TROPSCH (FT) SYNTHESES.

The FT synthesis dates back to 1923 with the discovery of a
catalyst to convert synthesis gas to hydrocarbon mixtures. Based
on this discovery, an industry was developed in Germany for the
conversion of coal-based synthesis gas to synthetic fuels (45).
The economic justification for this industry collapsed with the

end of World War II, when inexpensive oil became available. In the early fifties, a natural gas-based FT plant was built in Brownsville, Texas. Unfortunately, economic factors forced the shut down of the plant before sustained continuous operations could be achieved (18). At about the same time, new markets opened up for industrial and household use of natural gas by the construction of long distance pipelines, which eliminated the economic need for a FT conversion plant. However, the German and the American technological advances were utilized and further developed by South Africa where a giant coal-based synthetic fuels and chemicals industry was established (46-49). The rest of the world had very little interest in FT chemistry in the post war era until the energy crises of the seventies. These events rekindled research and development interests. Now the technology is approaching the status when natural gas conversion to liquid fuels and chemicals can be accomplished in commercially viable operations under specific circumstances. In 1993, Shell Intl. Gas Ltd has started up a large conversion plant in Malaysia, using their proprietary new technology (19). Also, since 1993, Mossgas in South Africa has been converting offshore gases to fuels using Sasol's fixed fluid bed technology (50).
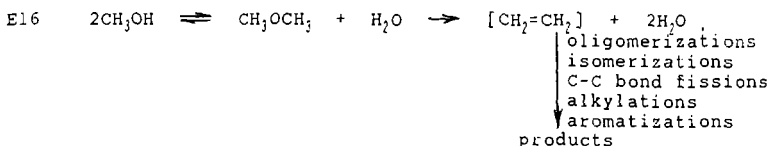
The FT chemistry and technology has numerous ramifications. Only some very basic concepts will be reviewed here. E14 illustrates the basic chemistry. The reaction can be considered as a polymerization reaction of C1 intermediates. A broad range of

E14 $\quad nCO + 2nH_2 \longrightarrow (CH_2)_n + nH_2O \quad \Delta H = -40$ kcal/mole CO

E15 $\qquad C_n = (\ln^2 \alpha)\, n\, \alpha^n$
     where C_n is the carbon selectivity of the product having n carbon number and α is the probability of growth.

products is obtained which are defined by a single parameter, the chain-growth probability or alpha according to the Anderson-Schulz-Flory (ASF) kinetic scheme (see E15). To-day a good qualitative understanding exists about the factors which can cause deviations from the ASF kinetics (51). In E14, the products are formulated as olefins. While the primary products are, indeed, predominantly olefins, the olefins may hydrogenate to paraffins in secondary reactions. A variety of oxygenated products also forms to some extent. Furthermore, the water gas shift reaction (E4) is also a side reaction. E14 is not limited by equilibrium. Ru, Ni, Fe, and Co catalyze the reaction; the latter two are the commercial choices. The Fe catalyst are usually unsupported, but they need alkali metal and other promoters and also require operations under pressure. They can be used in a wide temperature range (200-350°C). Co is more active than Fe. It also shows greater hydrogenation tendency for paraffin formation. The exothermic heat of the FT reaction is very high, requiring well controlled heat removal. With Fe catalyst, there is a wide choice for reactor and process design: fixed bed, circulating fluid bed, fixed fluid bed and slurry bed. For Co catalysts, to date only fixed bed operations were found satisfactory. Kinetic studies have amply demonstrated that the catalytic activity is limited by diffusion (51-53).

GASOLINE VIA METHANOL. THE METHANOL TO GASOLINE (MTG) PROCESS.

As an offshoot of the pioneering work on synthetic zeolites, it was discovered in Mobil Oil's laboratories, that methanol can be converted to a variety of hydrocarbon products over ZSM-5 zeolite (54,55). E16 illustrates the types of reactions occurring.

E16 $\quad 2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \longrightarrow [CH_2=CH_2] + 2H_2O$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ oligomerizations
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ isomerizations
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ C-C bond fissions
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ alkylations
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ aromatizations
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ products

Ethylene is indicated as an intermediate, though this mechanistic assumption is debated. The products are mixtures of olefins, isoolefins, isoparaffins and aromatics with less than 11 carbon per molecule. The product slate can be varied within certain

limits because the relative rates of the indicated reactions
vary, aromatization being the slowest. Subsequently processes
have been developed for high octane gasoline production from
methanol. A fixed bed process version was commercialized in 1986
in New Zealand for the conversion of natural gas to premium grade
gasoline (28,29).

COMPARATIVE ECONOMICS. OPPORTUNITIES FOR R&D.

Previous economic studies have clearly established that the large
capital requirement is the major obstruction to the evolution of
a natural gas-based synthetic fuel industry (19,56). Other
important factors are the cost (i.e. the local value) of the
natural gas, the quantities of fuel produced by the conversion
(i.e. the process efficiency) and the market value of the fuel or
chemicals produced. Table 1 compares salient economic features of
the natural gas conversion technologies, assuming 100 MMscft/day
natural gas usage. For the ammonia, methanol and syncrude
technologies, it can be assumed that the capital cost
requirements are approximately the same, hence the production
volumes and the product heating values are directly related to
the economics of these processes. The gasoline via methanol
conversion has higher capital requirements because of the extra
MTG process step.

Table 1. Comparison of Conversion Technologies, 100 MMscft/d Gas.			
Technology	% Process efficiency	Daily production quantities	
		Weight (tons)	Heating Gkcals
Ammonia (old)	69	3357	-
Ammonia (new)	82	3985	-
Methanol	78	3154	16.8
via combined reforming	85	3437	18.4
Syncrude (Shell MDS)	80	1414	16.2
Syncrude (possible)	88	1557	17.8
Gasoline (via methanol)	76	1317	14-15

For syncrude synthesis, 80% methane-based process efficiency is
estimated from the data reported by Shell. While this is a high
value, with advances much higher efficiency is possible for the
following reasons: All the gaseous products from the FT reactor
can be recycled into synthesis gas generation and hence 100%
liquid selectivity is possible. Furthermore, energy requirements
(for compressors, etc.) in the FT process are less than in
methanol synthesis while more energy is produced in the reaction.
Hence higher process efficiencies and lower capital requirements
may be possible in the FT process. Comparing methanol and
syncrude, it is apparent that methanol is a much preferred
product over syncrude because of its quantity. However, this
statement is valid only if methanol can be marketed for chemical
use. For the fuel market, methanol and syncrude product values
are nearly equal on the basis of their heating values.

To make the syncrude process viable, the simplest possible
process must be assembled, requiring the lowest amount of
capital. Furthermore, search must go on to enhance the value of
the syncrude fractions. It is already known, that syncrude
commands a premium price, because it is practically free of S and
N; its Diesel fraction has high cetane value and its wax
fractions have high chemical values. In Figure 3 a process scheme
is shown for staged coproduction of methanol and syncrude. This
seems feasible because there is an overlap around 450-500 psi
where syngas generation, methanol synthesis and syncrude
synthesis all could be accomplished. With coproduction of
methanol, the quantity and the value of the products are
increased. Substantial reduction of the capital requirements of
the syncrude process may be possible by making synthesis gas by
an energy efficient combined reforming technology similar to that
used in the ammonia industry, with air as the oxidant. In this
case, the research challenge is the efficient and selective
conversion of the nitrogen-diluted synthesis gas. It may be
possible to control the probability of growth in the FT synthesis
around 0.82, resulting in high selectivity to liquids (see Figure
4). This would eliminate the need for hydrocracking of the heavy
paraffins which is the current practice. Yet another opportunity
for capital reduction and improving the process efficiency could
be the introduction of efficient plate exchangers for heat

exchange duties, including in the design of the reactors. Of course, FT catalyst selection and design need to pay special attention to minimize the diffusional limitations.

Figure 3. MeOH-Syncrude Process.   Figure 4. MWD at 0.82 Alpha.[a]

gases

| Combined reforming | MeOH synthesis | Syncrude synthesis |

MeOH   Syncrude
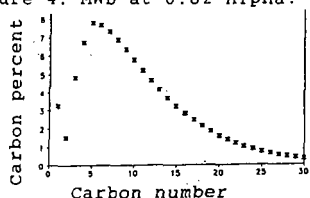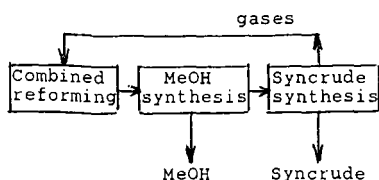
[a]Co catalyst. See reference 57.

In conclusion, the natural gas conversion technology to synthetic fuels offers the best opportunities for advances. Some approaches to reduce the capital requirements and simultaneously improve the process efficiency and product values have been outlined. Development and demonstration of these opportunities may lead to commercially attractive natural gas conversion even at the current oil price environment, if natural gas is available at low cost.

REFERENCES.

1 J.R. Rostrup-Nielsen, Catalysis Today, 21, 257 (1994).
2 J.M. Fox, Cat.Rev.-Sci.Eng., 35, 169 (1993).
3 G.A. Mills Paper C43, 13th North American Meeting of the
  Catalysis Society, May 2-7, 1993, Pittsburgh, PA. See also
  Idem, DOE, Nat. Renewable Energy Lab, HZ 1-11208-1 (1992).
4 J.L.G. Fierro, Catal. Lett. 22, 67 (1993).
5 J.H. Lunsford, Catalysis Today, 6, 235 (1993).
6 J.C.W. Kuo, C.T. Kresge and R.C. Palermo, Catalysis Today, 4,
  463 (1989).
7 T.A. Czuppon, S.A. Knez and J.M. Rovner in Encyclopedia of
  Chemical Technology, Fourth Ed. Vol.2, p.638. Wiley 1992.
8 J.R. Rostrup-Nielsen in Catalysis Science and Technology, J.R.
  Anderson and M. Boudart, Eds., Vol.5, p.1, Springer 1984.
9 J.P. Van Hook, Catal.Rev.-Sci.Eng. 21, 1 (1980).
10 F.E. Biasca, R.L. Dickenson, A.J. Moll, E.D. Oliver, D.R.
  Simbeck, Synthesis Gas for Chemicals and Fuels. Technology,
  Economics and Market Outlook. SFA,Inc. Final Report, October
  1983.
11 J.D. Fleshman, Chem.Eng.Progr., October 1993, p.20.
12 J.R. LeBlanc, Energy Progress 5 (1), 4 (1985).
13 J.R. Rostrup-Nielsen in Catalyst Deactivation, C.H.
  Bartholomew and J.B. Butt,, Elsevier, 1991. See also
  Idem, J.Catal., 85, 31 (1984).
14 N.R. Undergaard, J-H.B. Hansen, D.C. Hanson and J.A. Stal,
  Oil&Gas J., March 9, 1992, p.62.
15 S. Teuner, Hydr.Proc,, May 1985, p. 106 and July 1987, p.52.
16 H-J. Toepfer, GWF-Gas/Erdgas, 117, 412 (1976).
17 Prettre, Ch. Eichner and M. Perrin, Trans.Far.Soc., 42, 335
  (1946).
18 Anonymous, Chem.Eng.Progr., 53 (10), 1957, p.50.
19 P.J.A. Tijm, Preprint, Fuel Division, ACS, 39, 1146 (1994).
20 S.S. Bharadwaj and L.D. Schmidt, J.Catal., 146, 11 (1994) and
  references cited therein.
21 J.B. Huttl, Eng.& Mining J., 162 (7), 82 (1961).
22 H. Sachsse, Chem.-Ing.-Technik, 21 (1/2), 1 (1949).
23 Anonymous, Chem.Eng. July 9, 1962, p.38.
24 E. Supp, Hydr.Proc., July 1984, p.43-C.
25 D. Kitchen and A. Pinto, Ammonia Plant Safety, 31, 219 (1991).
26 H-D. Marsch and N. Thiagarajan, Ammonia Plant Safety, 33, 103,
  (1993).
27 P. Orphanides, Ammonia Plant Safety, 34, 292 (1994).
28 J. Haggin, C&EN, June 22, 1987, p.22.
29 C.J. Maiden, Chemtech, January 1988, p.38.
30 N. Shannahan, Hydr.Proc., January 1989, p.60.
31 S.A. Knez, D.O. Moore and R.V. Schneider, Kellogg Ammonia Club
  Meeting, San Diego, CA, August 1990.

32 M.D. Jackson and Carl B. Moyer in Encyclopedia of Chemical
   Technology, Fourth Ed., Vol.1, p.826, Wiley, 1991.
33 E. Supp, How to Produce Methanol from Coal. Springer, 1990.
34 K.C. Waugh, Catalysis Today, 15, 51 (1992).
35 G.C. Chinchen, J.P. Denny, J.R. Jennings, M.S. Spencer and
   K.C. Waugh, Appl.Catal., 36, 1 (1988).

36 J.C.J. Bart and R.P.A. Sneeden, Catalysis Today, 2, 1 (1987).
37 K. Klier in Advances in Catalysis, Eds. D.D. Eley, H. Pines
   and P.B. Weisz, Vol.31, p.243, Academic Press, 1982.
38 D.L. Trimm and M.S. Wainwright, Catalysis Today, 6, 261 (1990)
39 R.A. Koeppel, A. Baiker and A. Wokaun, Appl.Catal.A:General,
   84, 77 (1992).
40 D.M Brown, B.L. Bhatt, T.H. Hsiung, J.J. Lewnard and F.J.
   Waller. Catalysis Today, 8, 279 (1991).
41 J.M. Berty, C. Krishnan and J.R. Elliott, Chemtech, October
   1990, p.624.
42 K.R. Westerterp, M. Kuczynski and C.M.M. Kamphuis, Ind.Eng.
   Chem.Res., 28, 763 (1989).
43 J.B. Hansen and F. Joensen in Proc. Nat. Gas Conversion
   Symposium, Oslo, Aug.1990, p.457, Elsevier, 1991.
44 S.G. Neophytides and G.F. Froment, Ind.Eng.Chem.Res. 31, 1583
   (1992).
45 H.H. Storch, N. Golumbic and R.B. Anderson, The Fischer-
   Tropsch and Related Syntheses, Wiley, 1951.
46 M.E. Dry and H.B.deW. Erasmus, Ann.Rev.Energy, 12, 1 (1987).
47 M.E. Dry in Catalysis Science and Technology. Eds. J.R.
   Anderson and M. Boudart, Vol.1, p.159. Springer, 1981.
48 M.E. Dry, Catalysis Today, 6, 183 (1990).
49 B. Jager, M.E. Dry, T. Shingles and A.P. Steynberg, Catal.
   Lett. 7, 293 (1990)
50 Anonymous, Oil&Gas J., Jan.20, 1992, p.53.
51 R.S. Hurlbut, I. Puskas and D.J. Schumacher, This Symposium.
52 M.F.M. Post, A.C. van`t Hoog, J.K. Minderhoud and S.T. Sie,
   AIChE Journal, 35, 1107 (1989).
53 R.B.Anderson, J.F. Shultz, L.J.E. Hofer and H.H. Storch,
   Bulletin 580, Bureau of Mines, US Govmnt. Printing Office,
   1959.
54 S.L. Meisel, J.P. Mc Collough, C.H. Lechthaler and P.B. Weisz,
   Chemtech, February 1976, p.86.
55 C.D. Chang and A.J. Silvestri, J.Catal., 47, 249 (1977).
56 D. Gray and G. Tomlinson, Coal Liquefaction and Gas Conversion
   Contractor`s Review Conference, Sept, 7-8, 1994, Pittsburgh.
57 I. Puskas, R.S. Hurlbut, R.E. Pauls, J.Catal., 139, 591 (1993)